THE

ONTARIO WATER RESOURCES

COMMISSION

OUTLINES

of

ANALYTICAL METHODS

DIVISION OF LABORATORIES

OUTLINES OF ANALYTICAL METHODS

Compiled by

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CHEMISTRY BRANCH

DIVISION OF LABORATORIES

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INTRODUCTION

Information on analytical methods is often required in order to correctly interpret data and in the preparation of reports. This collection of outlines of analytical procedures has been prepared in order to provide some pertinent information in a brief non-technical form. The outlines are not intended to be guides for performing the analyses.

Descriptions of our most common tests are included, together with lists of sample volumes required and sampling supplies available. Similar information for most of the other tests carried out at our laboratories can be obtained by contacting the Division of Laboratories of the Ontario Water Resources Commission.

The individual test descriptions will be revised periodically as improvements are made in methods, accuracy and precision.

CONTENTS

Sample Volumes, Chemistry I

Sample Volumes, Chemistry II

Shipping Procedures

Sample containers and Supplies

Alkalinity

Aluminum

Arsenic

Biochemical Oxygen Demand

Calcium - see Hardness

Cadmium

Total and Organic Carbon

Chemical Oxygen Demand

Chloride

Chromium

Conductivity (specific conductance)

Color

Copper

Cyanide

Detergents - Anionic

Ether Extractables - Oils & Greases

Fluoride

Hardness - Calcium-Magnesium

Contents (page 2)

Herbicides - Chlorophenoxy Acetic Acid type
- Triazine

Iron - Total

Ketones

Lead

Magnesium - see Hardness

Manganese

Nickel

Nitrite Nitrate as Nitrogen

Ammonia & Kjeldahl Nitrogen

Pesticides - Chlorinated Hydrocarbon

Potassium - see Sodium

pH

Phenols

Phosphorus - Soluble

Phosphorus - Total

Silica

Sodium & Potassium

Solids - Total Suspended & Dissolved

Tannins & Lignins

Turbidity

Zinc

Sample Volume Required for Regular Analyses

Chemistry I Branch

A 32-ounce bottle contains sufficient sample for a routine chemical examination of water (hardness, alkalinity, chlorides, iron and pH), or of sewage (BOD, solids and/or turbidity).

There are a few tests which require a fixed volume of sample, almost irrespective of sample strength. For methods currently in use, these include:

	Metric Volume Required	Approximate Ounce Equivalent
Total Solids -	100 mls	(3½ ounces)
Turbidity -	150 mls	(5 ounces)
Conductivity -	200 mls	(7 ounces)
pH -	25 mls	(1 ounce)

For the great majority of tests, however, the volume required is dependent on sample strength, with 'weaker' or clean samples, such as drinking waters and unpolluted well and surface waters, requiring the largest volumes. For a sample containing low concentrations of a substance, the largest practical volume is tested in order to obtain a sufficient quantity of the substance to detect reliably. For stronger samples, such as effluents and sewage, a smaller amount, or even a dilution, can often be employed.

The table below lists the lower ranges of concentration which can be detected and the sample volume required to analyze in this range. This volume is thus the maximum usually needed. For stronger samples, the volume can be reduced in rough proportion to the expected strength. Since this is a matter of judgment on the part of the sampler, we would ask that the sample be sized on the generous side. It is of advantage to have a remnant of the sample available after all tests have initially been set up. This remnant should be about one-fifth of the sample or, at least, six ounces. This allows two important laboratory verifications to be performed. If the volume of sample chosen for a test is discovered to have been inappropriate to the strength of the sample, this is usually discovered early in the test, and the test can then be repeated using a more informed choice of test volume, if surplus sample is available. In addition, following completion of all tests, the results are reviewed to detect any calculation errors, uncertainty as to the identity of the sample, etc. It is of great assistance to have sufficient sample left to provide visual confirmation of its quality in comparison with the results obtained.

Test	Low Concentration Range ppm				Sample Volume Required Metric.	Approximate Imp. Ounce Equivalent
Anionic Detergents	0.1	-	2.0		125 mls.	4.5 ounces
BOD_5	1.	-	10.		500 mls.	18 ounces
COD	50.	-	800.		75 mls.	3 ounces
NUTRIENTS						
Total Phosphorus	0.00	-	0.20	P	→ 75 mls.	3 ounces
Kjeldahl Nitrogen	0.01	-	1.0	N		
Soluble Phosphorus	0.00	-	0.20	P		
Ammonia	0.01	-	1.0	N	→ 75 mls.	3 ounces
Nitrite	0.00	-	0.20	N		
Nitrate	0.01	-	2.0	N		
Suspended Solids	2.	-	20.		400 mls.	14 ounces
Alkalinity	2.	-	800.		75 mls.	3 ounces
Calcium, Magnesium	1.	-	200.		75 mls.	3 ounces
Chlorides	1.	-	400.		75 mls.	3 ounces
Fluoride	0.1	-	2.0		350 mls.	12 ounces
Hardness	5.	-	1000.		75 mls.	3 ounces
Iron	0.05	-	2.5		75 mls.	3 ounces
Sodium, Potassium	0.1	-	25.		75 mls.	3 ounces
Sulphate	10.	-	200.		250 mls.	9 ounces

If one bottle is insufficient to provide an ample volume, then two bottles should be collected, labeled identically, and both should be marked "Duplicate Sample".

Volumes required for other Chemistry I Branch tests should be ascertained by enquiry - telephone 248-3064-5.

Inorganic Tests Performed by Chemistry II Branch.

Common Heavy Metals	Range (ppm)	Aliquot Req. (ml.)	Equivalent Aliquot (oz.
Aluminium	0.01 - 0.20	200	8
*Cadmium	0.01 - 50	400	15
Calcium	0.09 - 10	200	8
Chromium	0.05 - 1.0	200	8
*Cobalt	0.10 - 10	200	8
*Copper	0.08 - 10	200	8
*Iron	0.10 - 10	200	8
Lead	0.18 - 20	200	8
Magnesium	0.01 - 1.0	200	8
Manganese	0.04 - 5.0	200	8
*Nickel	0.10 - 15	200	8
*Zinc	0.01 - 2.0	200	8

Other Heavy Metals	Range (ppm)	Aliquot Req. (ml.)	Equivalent Aliquot (oz.
Antimony	0.1 - 20	400	15
Barium	2 - 100	1000	40
Boron	0.05 - 2.0	200	8
Mercury	0.01 - 1.0	400	15
Molybdenum	0.06 - 10	400	15
Selenium	0.05 - 100	1000	40
Silver	0.04 - 5.0	200	8
Tellurium	0.01 - 50	400	15
Tin	0.1 - 5.0	400	15
Titanium	0.15 - 10	200	8
Vanadium	0.05 - 10	200	8

*These elements can all be determined in a single 400 ml. aliquot. The ranges can usually be extended by dilution or concentration of the sample.

NOTE: The most accurate analyses for metals are obtained from samples collected in plastic bottles and acidified with nitric acid. No acid is to be added if the "soluble" fraction is also to be determined. Glass bottles with plastic caps are acceptable for all metals except MERCURY, SILVER AND TIN which tend to plate out on glass; therefore, samples for these tests must be collected in plastic bottles.

Foil-lined caps should be avoided as they contain aluminium, tin, lead and copper, which may contaminate the sample and invalidate determination of these metals. If foil-lined caps are used, then the sample should not be acidified in any case.

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Anions	Range (ppm)	Aliquots Req.(ml.)	Equivalent Aliquot (oz.)
Arsenic	0.01 - 1.0	200	8
Cyanide	0.01 - 2.0	1000	40
Silica	0.02 - 2.0	100	4
Sulphide	0.1 - 5.0	200	8
Sulphite	>0.1	100	4

NOTE: Samples should be collected in glass bottles and rendered basic by adding sodium hydroxide.

Samples for sulphide analysis should be preserved by adding both sodium hydroxide and zinc acetate.

The ranges can usually be extended upward only, by dilution of the sample.

General Tests	Range (ppm)	Aliquot Req.(ml.)	Equivalent Aliquot (oz.)
Chlorine Demand	>0.5	200	8
Iodine Demand	>0.1	100	4
Lignins & Tannins	0.5 - 5.0	100	4
Pearl-Benson Index	0.0025 - 0.20%	100	4
Threshold Odour		500	20

NOTE: Samples for these analyses may be collected in glass bottles.

Do not use any preserving agent, but refrigerate the sample, if possible, and submit for analysis as soon as possible.

The ranges can usually be extended upward only, by dilution of the sample.

ALL VOLUMES GIVEN ARE SUFFICIENT FOR DUPLICATE ANALYSES.

A GUIDE TO SHIPPING PROCEDURES

RAIL EXPRESS: The correct shipping address is:

OWRC Laboratories,
Resources Road,
Hwy. 401 and Islington Avenue,
Rexdale, Ontario.

Pre-addressed labels may be obtained from the Traffic Section at 248-3027. Put the sender's name, point of origin, weight (if known), and the number of cartons or boxes in the shipment on the label. Use "Perishable Goods" label when applicable and remove or erase any old labels.

Indicate whether the shipment is "Collect" or "Prepaid". Shipments which can be identified as being from OWRC staff members are accepted on a "Collect" basis. All other shipments must be prepaid. Exceptions are made for samples submitted by others at the request of the OWRC staff; however, Traffic Section must be notified in advance in writing, otherwise the shipment will not be accepted.

Keep a copy of the weigh-bill receipt for three months, since it is needed for tracing lost shipments or claiming damages for broken bottles and cases.

Include "Request for Laboratory Analysis" forms and make sure that the numbers on the forms agree with those on the bottles. These forms are placed in the empty cases and are also available from the Traffic Section, along with waterproof envelopes. When sending in water samples for both chemical and bacteriological analyses, please include duplicate copies of the analysis forms.

AIR EXPRESS:

Air Express is fast but very expensive and should only be used in essential cases and with the authority of the branch supervisor. Delivery from the airport to the laboratories is made automatically without delay or additional charges.

AIR FREIGHT:

Air Freight should be avoided, as it is costly and often no faster than rail express. Delivery is to the airport only and there are additional charges and delays in getting the samples to the laboratories.

ROAD TRANSPORT or BUS LINE:

These methods of shipment should be avoided, as final delivery to the laboratories is unreliable and sometimes slow. If a bus line is used, please arrange for pickup service from the bus terminal. The OWRC often has difficulty in arranging reimbursement of small amounts to the various transport companies.

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MAIL: The correct mailing address is:

OWRC Laboratories,
P.O. Box 213,
REXDALE, Ontario.

The mailing of full 32-oz. bottles is strictly forbidden by the postal authorities. Full 6-oz. bacteriological bottles are not willingly accepted by the post office.

GENERAL NOTES:

Please notify the OWRC Traffic Section at once if a shipment is lost and give very specific shipping details so that prompt recovery can be made.

Allow at least three days for shipment of containers to the Lakehead, two days for Cochrane, and one day for shipment to most southern points.

When advance orders have been made for containers to be shipped marked "hold until called for", please inform the Traffic Section immediately if they cannot be picked up. The Traffic Section will then take steps to recover them from the railway companies.

Avoid over-stocking and return unused containers promptly. If 30 boxes are needed over a three-week period, it is better to request 10 boxes each week rather than 30 at once. The OWRC has over 900 wooden sample cases and this is ample, provided that they continue to circulate. Wooden boxes are for the use of OWRC personnel only.

Weight Chart - These are the approximate weights of containers and should only be used when a weigh scale is not available.

Pack #	Size	Description	Bottles Full	Bottles Empty
1	1 x 32 oz	cardboard container	3½ lb.	1½ lb.
2	2 x 32 oz.	cardboard container	7 lb.	3 lb.
3	12 x 32 oz	carton (6 twin packs)	42 lb.	18 lb.
4.	4 x 32 oz	wooden box	22 lb.	15 lb.
5.	8 x 32 oz.	wooden box	42 lb.	22 lb.
6.	1 x 6 oz	mailing tube	1 lb.	½ lb.
7.	2 x 6 oz	mailing box	2 lb.	1 lb.
8	4 x 6 oz.	cardboard container	3½ lb.	2 lb.
9	6 x 6 oz	cardboard container	5 lb.	3 lb.
10	24 x 6 oz.	wooden box	32 lb.	24 lb.
11.	33 x 6 oz.	wooden box	42 lb.	30 lb.
12	92 x 6 oz.	carton (23 four packs)	82 lb.	45 lb.

When ordering supplies by telephone, ordering by "pack number" will be sufficient.

SAMPLE CONTAINERS AND SUPPLIES

The following items may be obtained from the Traffic Section; telephone Mr. Norm Partridge at 416-248-3027. If Mr. Partridge is absent, ask for Bill Scott, Shipper. When making requests by mail, please use an internal pink requisition slip:-

Pack #	Size	Description
1	1 x 32 oz	cardboard container
2	2 x 32 oz	cardboard container
3	12 x 32 oz	carton (6 twin-packs)
4	4 x 32 oz	wooden box
5	8 x 32 oz	wooden box
6	1 x 6 oz	mailing tube
7	2 x 6 oz	mailing box
8	4 x 6 oz	cardboard container
9	6 x 6 oz	cardboard container
10	24 x 6 oz	wooden box
11	33 x 6 oz	wooden box
12	92 x 6 oz	carton (23 four-packs)

(ORDERING BY PACK NUMBER WILL BE SUFFICIENT INFORMATION)

6 oz or 32 oz Orthotolidine in amber glass
32 oz Jars, Unity, wide mouth (sludge)
12 oz Jars, pomade, cylindrical
4 oz Jars, pomade (handy for powder chemicals)
1/2 gal. Jugs, Winchesters, glass, with handle
Pads of Laboratory analysis forms (100 per pad)

Please note that the mailman is not responsible for the transfer of boxes and cartons between the Laboratory and other OWRC buildings. Other pickup arrangements have to be made.

Equipment Store carries the following supplies:-

Fluoresceine dye, various coloured tracing dyes,
Rhodamine liquid dye, dissolved oxygen kit supplies,
chemical solutions - copper sulphate, starch, sulphuric acid in varied concentrations, sodium thiosulphate, formaldehyde, kemerrer samplers, rubber boots, rainwear, and varied field equipment of a non-expendable nature.

Telephone Ron Harrison at 416-248-3053

Main Stockroom - telephone 416-248-3049 - carries most other expendable supplies, including glassware, thermometers, filter papers, tapes and stationery, and ethyl alcohol, the latter being available in all sizes up to one gallon.

It would help to speed the filling of requisitions if Traffic, Equipment and Main Stockroom items are ordered on separate forms.

ALKALINITY

The alkalinity of a water sample is a measure of its capacity to neutralize acid. This capacity is the combined result of the carbonate, bicarbonate, and hydroxide content of the water.

Sampling

Conventional sampling equipment is satisfactory, but there should be no alkaline or acidic preservatives added, and the sample must not be frozen. The sample should be protected against temperature changes and from any other influences which might affect its pH.

Method

The sample is titrated with an acid solution of known concentrations until the pH is reduced to the methyl orange end-point (about pH 4). The alkalinity is then reported as ppm $CaCO_3$ and represents the concentration of $CaCO_3$ in ppm which would be required to react with the acid consumed in the titration.

Precision - ± 1 ppm

Accuracy - ± 3 ppm

Interpretation

While the results are reported in ppm as $CaCO_3$, this does not necessarily imply that there is this amount of $CaCO_3$ in the solution or that there is any there at all. The quantity measured is the amount of acid required to reduce the pH of a measured portion of the sample to 4.

In order to draw conclusions regarding the amount of a particular ion which may be present, it is necessary to refer to additional information from some other source such as the sample pH or its phenolphthalein alkalinity. In some cases, the reported result will have to be converted back to its acid equivalent and this result used for calculation.

Cost

A single routine measurement costs about one dollar.

References

Standard Methods, pages 48 to 52.

See page 51 for alkalinity relationships.

ALUMINUM

Aluminum is a very abundant element in nature and is widely distributed in soluble and insoluble forms. Aluminum compounds occur naturally in water, but may also derive from industrial wastes or from water-treatment plants. At present, there is no evidence that aluminum is physiologically harmful and no drinking water standard has been specified. The presence of small amounts of aluminum in water may interfere with certain industrial processes.

Sampling - The most reliable analytical result is obtained from a sample collected in a plastic bottle or in a glass bottle with a plastic-lined cap and acidified with nitric acid.

Method - Analysis is usually carried out on the sample without any pretreatment; however, if necessary, the aluminum can be converted to a form suitable for analysis by digesting the sample with a sulphuric-nitric acid mixture. Then the aluminum is determined by the colorimetric aluminon method or the chrome azurol-S method.

Precision and Accuracy

Method	Range of Application	Sensitivity	Accuracy	Precision
Colorimetric-(Aluminon)	0.01 - 0.20 ppm	0.01 ppm	5% (at 0.5 ppm level)	± 0.01 ppm
Colorimetric (Chrome Azurol-S)	0.005 - 0.20 ppm	0.005 ppm	5% (at 0.5 ppm level)	± 0.1 ppm

Notes: The aluminon test is preferred because of the excellent precision, accuracy and sensitivity it offers. Iron, phosphates and fluoride interfere, and if such species are likely to be present, the laboratory should be notified.

The chrome-azurol-S method is used in special cases requiring checks or the determination of very small amounts of aluminum.

Time of Analysis

A single analysis for aluminum requires about 3½ hours. However, sixteen analyses can be completed in a day if the samples are tested in batches.

If digestion is not necessary, a single analysis requires one hour, and 32 analyses per day can be completed.

Arsenic

Arsenic may occur in natural waters from dissolution of minerals, industrial discharges, and from application of insecticides. The element and its salts are highly toxic to humans and also have been identified as carcinogens. Since arsenic is eliminated only slowly from the body, it tends to accumulate, becoming concentrated in the nails and hair. Hence, the prolonged intake of water containing only minute quantities of arsenic may be detrimental to health. For this reason, the maximum permissible concentration in domestic water supplies has been established as 0.05 ppm, with an objective of less than 0.01 ppm.

Sampling

Preferably, the sample should be collected in a plastic bottle and acidified with nitric acid.

Method

In order to obtain the arsenic in a form suitable for analysis, the sample is first digested with a nitric-sulphuric acid mixture. Then the arsenic is reduced to arsine, AsH_3, and reacted with silver diethyldithiocarbamate solution in a modified Gutzeit generator to form a coloured compound. The concentration of arsenic is then obtained colorimetrically.

Precision and Accuracy

Method	Range of Application	Sensitivity	Accuracy	Precision
Colorimetric	0.01 - 0.5 ppm	0.01 ppm	10%	± 10%

NOTE: (1) The range of application can be extended by dilution or concentration of the sample.

(2) The figures given for accuracy and precision are average values. Deviations from these values are to be expected for very high or very low concentrations of arsenic.

(3) Several metals may interfere to a small extent with the generation of arsine, but the chief interference is antimony which will react with the colour reagent similarly to arsenic. The species measured by this test is the arsenic cation and the results are expressed as arsenic, (As).

Time of Analysis

A single analysis for arsenic by the colorimetric method requires about three hours. However, approximately fifteen analyses per day can be completed when the samples are tested in batches.

BIOCHEMICAL OXYGEN DEMAND (BOD)

The most frequent damage caused by the discharge of wastes to natural waters, next only to bacterial contamination, is the reduction of dissolved oxygen concentrations to levels which cannot support normal aquatic life. The resulting fish kills are accompanied by deterioration of the water quality for all uses. The dissolved oxygen is depleted through oxidation of the organic content of the wastes by bacteria (occasionally by direct chemical oxidation). The BOD test is a measure of the amount of dissolved oxygen required for the process of stabilization of the decomposable organic matter by aerobic bacterial action in a specific length of time (five days) under standard conditions. (20°C in the dark)

Sampling - Samples for BOD analysis are perishable and should be delivered immediately, preferably under refrigeration. Preservatives cannot be employed since they would retard bacterial action during the test procedure.

Method - A general description of the method is given in Standard Methods, beginning on page 415. The test is carried out by preparing dilutions of the original sample as necessary, and measuring the dissolved oxygen depletion in each after incubation in a sealed bottle for five days at 20°C. Specific optional equipment, techniques and criteria employed in the OWRC Laboratories include the following:

Flat-sided 175 'Prince of Wales' type bottles with screw caps are used for incubations. These occupy less shelf space and are convenient to handle in large numbers. A conical polyethylene liner, used inside the cap, allows the incubation bottles to be sealed without enclosing any air bubbles.

A number of dilutions of each sample are prepared, of which only those giving a five-day depletion of dissolved oxygen between 25 and 75% are accepted in calculating test results.

Initial dissolved oxygen concentraitons in duplicate portions of each dilution are measured by direct test, rather than being obtained by calculation.

A dropping mercury polarograph, based on the design of Briggs, is employed to measure dissolved oxygen, and is standardized by comparison with results obtained using the Winkler Method (1). Adequate precautions must be taken against mercury spillage and mercury vapour poisoning.

Among samples containing toxic substances, only those with adverse pH levels or chlorine residuals are corrected by pretreatment and seeding. Stale sewage is used as seed and the oxygen demand due to the seed is deducted. Such seeding is seldom relevant for other samples.

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Samples containing visible concentrations of algae are incubated in bottles painted black on the exterior to eliminate photosynthetic production of oxygen.

Precision - Routine laboratory measurements are generally reproducible to within ± 10%. Precision is seriously reduced if the sample contains large fragments of suspended solids, since reproducible and representative portions of such a sample cannot be withdrawn for analysis. Samples in this category can be homogenized in a Waring blender before an aliquot is taken, but this can increase the apparent BOD by rendering the solids more decomposable.

Accuracy - It is virtually impossible to define the accuracy of the BOD test except for pure organic compounds such as the glucose-glutamic acid standard solution (1). Techniques which give accurate results for these standards are assumed to give the "correct" BOD for a given waste.

Interpretation - While the BOD test remains the most useful test in assessing the strength of deoxygenating wastes and their potential polluting effects, there are cases, such as the presence of substantial quantities of toxic materials, in which the application of the test is limited. Factors to be considered in applying and assessing BOD results are discussed in (1) and (2).

When examining the effects of deoxygenating discharges, samples for BOD tests should be collected both above and throughout the affected area of the receiving water. In addition, these BOD tests should always be supplemented by on-site Dissolved Oxygen tests in order to assess the effects of stream conditions which offset or accentuate the tendency of the BOD of the waste to rob the receiving water of dissolved oxygen.

(1) Standard Methods for the Examination of Water and Wastewater - 12th edition.

(2) Chemical Aspects of River Pollution, Klein, published by Butterworth.

CADMIUM

Cadmium and its salts are used in metallurgy, electroplating and various other industries. All forms of this element are highly toxic, and, once ingested, are likely to remain in the body for a long time, becoming concentrated in the liver and other organs. The drinking water objective is 0.01 ppm, and a highly sensitive analytical method is therefore required.

Sampling - The most reliable analytical results are obtained on samples collected in plastic bottles and acidified with nitric acid.

Method - In order to obtain the cadmium in a form suitable for analysis, the samples are first digested with a nitric-sulphuric acid mixture. The cadmium is then determined by atomic absorption spectrophotometry (AAS) or polarography. A very sensitive colorimetric method is also available, but it is a complex technique requiring specially trained personnel and it is used for instrument calibration only.

Precision and Accuracy

Method	Range of Application	Sensitivity	Accuracy	Precision
Atomic Absorption	0.02 - 2.5 ppm	0.02 ppm	0.3%	± 0.34%
Polarographic	0.1 - 10 ppm	0.1 ppm	1%	± 2%
Colorimetric	0.01 - 1 ppm	0.01 ppm	10%	± 10%

NOTE: 1. The ranges of application can be extended by dilution or concentration of the sample

2. Cadmium is one of the elements most suited to analysis by AAS, as there are no known chemical interferences.

Time of Analysis - A single analysis for cadmium by the preferred atomic absorption method requires about three hours. However, 20 analyses per day can be completed when the samples are tested in batches. The colorimetric and polarographic methods require more time for completion and are used mainly for standardization and control purposes.

TOTAL AND ORGANIC CARBON

The organic content of water and waste waters and its effect on the oxygen content is usually measured by the Chemical Oxygen Demand (COD) and Biological Oxygen Demand (BOD) tests. Both of these indirect tests are subject to a variety of interferences. The Total Organic Carbon (TOC) test described here measures directly the total and inorganic carbon content of a liquid sample. The organic carbon content may be obtained by difference for any given compound or mixture. This TOC value will have a direct relationship with BOD and COD values. However, it is obvious that this relationship will vary with the composition of the organic material present. The test is rapid, and suitable for the evaluation of organic pollution levels, assessment of treatment procedure efficiencies, and for assisting assimilation studies.

Sampling - The test handles clear water samples most easily. It is necessary that any solid or suspended material should be in such a state as to be easily homogenized for injection. Samples should be taken in clean glass bottles with foil-lined caps. Samples should be cooled or frozen to prevent bacterial decomposition and loss of carbon as CO_2.

Method - The sample is burned on a hot catalyst and the CO_2 produced is measured by infrared absorption and comparison with a CO_2 standard cell.

Sensitivity - approx. 2 ppm (background factor from diluent)

Precision and Accuracy - ± 2%

Interpretation - The TOC test gives an accurate value for the organic carbon content in a relatively short time. The COD/TOC ratio is indicative of the type of organics present, just as the COD/BOD ratio is indicative of the biodegradability of the compounds present. For the same type of organics, these ratios remain constant. Thus, the rapid TOC test permits the indirect determination of COD and BOD in samples of a relatively constant composition. TOC may thus, in many cases, be an adequate parameter for measurement of organic pollution.

Since solid materials can cause discrepancies in results, it should be specified on submitting samples containing such material whether analysis for TOC is required on the homogenized sample or on the supernatant liquid.

Expenses - An average of 100 - 120 tests per week can be done by one technician. The actual analysis takes only a few minutes; the homogenization of samples is the time-consuming part of the test.

CHEMICAL OXYGEN DEMAND (COD)

The chemical oxygen demand determination measures the weight of oxygen which will react with a given waste material under vigorous chemical oxidation conditions. The test gives a rapid estimate of the strength of a waste and is particularly useful for industrial wastes on which the BOD test is not applicable as it may give false low results.

Sampling - Conventional sampling equipment is adequate. Refrigeration is a satisfactory method of preservation for most samples, but if there are unstable compounds present, then the analysis must be carried out soon after collection in order to obtain reliable results.

Method - The procedure recommended in Standard Methods* is used. The raw sample is boiled for two hours with a known amount of potassium dichromate and sulphuric acid. Silver sulphate is used as a catalyst and mercuric sulphate is added to prevent interference by chloride. The dichromate remaining after boiling is titrated with standardized ferrous ammonium sulphate solution. The weight of oxygen taken up by the waste is calculated from the initial and final amount of dichromate in the mixture. The results are reported in mgms of oxygen consumed per liter of sample.

Precision and Accuracy - The test can be applied to samples in the range of 50 to 2000 mgm/liter, with a precision of ± 5% and an accuracy of ± 10%. Results below 50 mgm/liter can only be obtained as a rough estimate. As it is difficult to get representative aliquots from multiphase samples, the accuracy may be considerably less for such wastes. Precautions to prevent the interference by chloride are often only partially successful in the presence of high chloride concentrations.

Interpretation - Most organic compounds are oxidized by the test, benzene, toluene and pyridine being the common exceptions. The silver catalyst aids in oxidizing straight chain compounds. The results do not necessarily relate directly to the BOD value or to the oxygen consumption in the receiving water. They do represent a maximum carbonaceous oxygen demand which might ultimately be exerted in the water through time. Variations in COD from time to time at a given sampling location, or for a given effluent, may be more important than the absolute value of individual measurements. If comparative analyses show that a stable ratio exists between COD and BOD in a particular case, the COD results can then be used to predict the approximate BOD values. A single determination costs about three dollars.

*Standard Methods for the Examination of Water and Wastewater, 12th edition, American Public Health Association Inc., New York. 1967.

CHLORIDE

Chloride ion is a principal anion in domestic wastes and in many natural water supplies. Urban runoff often contains high concentrations of chloride in the winter time due to the application of salt (sodium chloride) to roads for ice control. It does not pose a direct health hazard, and the drinking water standard of 250 mgms per liter has been set to prevent water supplies from having a "salty" taste. High chloride concentrations promote corrosion of plumbing.

Sampling - Conventional sampling equipment is adequate. Chloride is one of the most stable parameters routinely measured and no preservation procedures are required.

Method - The chloride is titrated with a standardized silver nitrate solution. The titration is carried out automatically on a titralizer instrument which detects the titration end-point potentiometrically rather than by the chromate indicator described in Standard Methods.*

Precision and Accuracy - Chloride concentrations in the range of 1 to 400 mgms per liter (ppm) can be measured with a usual accuracy and precision of ± 2 mgms per liter. Both the accuracy and precision increase (± 1 mgm per liter) for low concentrations in "clean" water and decrease for high concentrations (greater than 400) in more "polluted" samples where interference by other components is likely.

Cost - A single chloride determination costs less than one dollar.

*Standard Methods for the Examination of Water and Wastewater, 12th edition, American Public Health Association, Inc., New York. 1967.

CHROMIUM

Hexavalent chromium salts are used extensively in the plating industries, tanneries, and in the manufacture of paints and dyes. Industrial uses for trivalent chromium are more limited. The presence of chromium in water will probably be the result of one of these industrial discharges or the result of the discharge of cooling waters in which chromium has been used as a corrosion inhibitor. Hexavalent chromium is the more toxic form and has been cited as a carcinogen; therefore, the maximum permissible concentration in domestic water supplies has been established as 0.05 ppm.

Special Sampling Instructions - Samples for total chromium analysis should be collected in plastic bottles and acidified with nitric acid. However, samples in glass bottles with plastic-lined caps are accepted. If the hexavalent chromium concentration is to be measured, then the sample must not be acidified. In all cases, the bottle should be filled to the top.

Method - For a total chromium analysis, the sample must first be digested with sulphuric and nitric acids and hydrogen peroxide; then the chromium is oxidized with permanganate to the hexavalent form. Once in this form, the chromium concentration can be determined by colorimetry or atomic absorption spectrophotometry (AAS). Hexavalent chromium is determined directly, using a colorimetric method, with no sample pretreatment other than filtration.

Precision and Accuracy

Method	Range of Application	Sensitivity	Accuracy	Precision
Colorimetric	0.05 - 0.4 ppm	0.05 ppm	1%	± 1%
Atomic Absorption	0.12 - 10 ppm	0 12 ppm	1%	± 1%

NOTES:
1. The ranges of application can be extended by dilution or concentration of the sample.
2. The colorimetric method is preferred over AAS because of the superior sensitivity.
3. High chloride, vanadium, iron, and mercury concentrations affect the colorimetric test.

Time of Analysis - A single analysis for total chromium by the preferred colorimetric method requires about one day. However, approximately 18 analyses per day can be completed when the samples are tested in batches. The atomic absorption method requires approximately the same amount of time. Hexavalent chromium alone is easily determined in about fifteen minutes.

SPECIFIC CONDUCTANCE

The specific conductance of a solution is the reciprocal of its electrical resistance measured between two electrodes 1 cm square and 1 cm apart. The current is carried by the ions in solution and both their nature and concentration affect the conductance. A temperature change of 1°C will affect the conductance by about 2% and for this reason all results are referred to a standard temperature, usually 25°C.

While the specific conductance depends on the total dissolved solids, there is no universal factor for converting one measurement to the other. In order to do this, it is necessary to determine the exact relationship for any given situation. For Ontario rivers, free of industrial wastes, total dissolved solids is equal to 0.65 ± 0.10 times the conductivity. Conductivity measurements have largely replaced the total dissolved solids test because they are more precise, particularly at low concentrations.

Sampling

Specific conductance is a stable parameter and the two main precautions are to avoid contact with any material which can release or adsorb ions and to prevent the sample from freezing. Some carbonates are precipitated on freezing and are not easily redissolved.

Method

The electrical resistance of the sample is measured by a conductivity meter which takes the reciprocal automatically. This result is multiplied by a cell calibration factor to compensate for the fact that the electrodes are not exactly 1 cm square or 1 cm apart. Measurements are made at ambient temperature (usually 20°C or greater) and a temperature correction factor is applied. The temperature correction is obtained from a pure KCI solution. The specific conductance of natural waters usually has a slightly greater temperature coefficient, and if the temperature is far from 25°C, an error is introduced by the large and not completely accurate correction.

The results are reported as micromhos/cm or just micromhos.

Accuracy and Precision

Accuracy and precision are from ± 1 to 5 percent, with the error increasing as the conductance decreases. This means that it is impossible to detect changes in concentrations of 1 or 2 ppm unless the total conductance is 10 micromhos or less.

Interpretation of Results

The conductivity of natural waters is mainly due to the presence of Ca, Mg, Na, Cl-, carbonate and bicarbonate ions. Organic compounds which remain unionized have little or no effect. The common pollution parameters such as nitrogen and phosphorus are usually present at concentrations too low to be accurately detected

Cost - A single determination can be made for less than one dollar.

COLOR

Many lakes and rivers, especially in Northern Ontario, have a characteristic brownish color due to the presence of "humic acid" derived from the decomposition of plants. Colored water, although harmless, is not appealing to drink, and an objective of 5 color units has been adopted for drinking water.

Many industrial effluents, particularly those from pulp and paper mills, are highly colored and their presence in the receiving water can often be traced by color measurement.

Sampling - The color of lake and river water is normally stable, and conventional sampling equipment is adequate. The color of effluents is less stable, but samples will usually arrive at the laboratory by normal shipping methods in time for satisfactory results to be obtained.

Method - The sample is compared to a series of standard color disks of matching hue which are calibrated in Hazen units (named after the originator). The comparison is made in an optical instrument (Lovibond Color Comparator). The laboratory normally determines the "apparent color" since this is the trait by which a consumer judges the water. Apparent color includes both the "true" color present in solution and the additional color contributed by suspended matter.

Very turbid samples are allowed to settle prior to color measurement. These results approximate the "true" color and a note to this effect is included with the reported values.

Cost - A single color measurement costs about one dollar.

Copper

Copper salts, found in natural waters, are generally the result of pollution from any of a wide variety of industries. They impart a disagreeable taste at concentrations well below those which would be hazardous to health. Hence, the choice of a drinking water objective of 1.0 ppm is based on taste rather than on toxicity.

Sampling

The sample should preferably be collected in a plastic bottle and acidified with nitric acid. However, no acid should be added if both dissolved and suspended forms are to be determined.

Method

In order to obtain the copper in a form suitable for analysis, the sample is first digested with a nitric-sulphuric acid mixture. The copper is then determined by atomic absorption spectrophotometry, colorimetry, or polarography.

Precision and Accuracy

Method	Range of Application	Sensitivity	Accuracy	Precision
Atomic Absorption	0.08 - 10 ppm	0.08 ppm	1.1%	± 1.1%
Colorimetric	0.15 - 20 ppm	0.12 ppm	2 %	± 2 %
Polarographic	0.05 - 10 ppm	0.05 ppm	5 %	± 5 %

The atomic absorption method is preferred because it is faster than the others and more accurate. High concentrations of sodium or potassium (0.5% or more) interfere with the method and, if such concentrations are suspected, a note to this effect should be put on the sample label.

Time of Analysis

A single analysis for copper by the preferred atomic absorption method requires about three hours. However, twenty analyses per day can be completed when the samples are tested in batches. The colorimetric and polarographic methods require more time for completion.

Cyanide

Simple cyanides and some complex cyanides dissociate in aqueous solution to yield the cyanide ion, CN^-, which is highly toxic. Many heavy metal complex cyanides are not toxic themselves but may break down under certain conditions to release free cyanide. The extremely high toxicity of cyanide made it necessary to set the drinking water objective to 0.01 ppm and to employ a test which is sensitive in this low range.

Sampling

A separate 40-oz. glass bottle of sample is preferred, since a single test normally requires a 500 ml. sample aliquot. The pH of the sample should be adjusted to about 11 with sodium hydroxide, and the sample should be refrigerated during transit.

Method

In order to eliminate most of the possible interferences, all samples received for analysis of cyanide are subjected to a preliminary screening procedure consisting of one of the following distillation methods:

1. If an analysis for the simple or "free" cyanide is required, the sample is distilled from a weakly acid solution. (Tartaric acid distillation.

2. If a total cyanide analysis is required, the sample is distilled under reflux from a solution containing strong acid and metal salts. (Serfass distillation).

Cyanide in the distillate is determined by two methods, the choice of method being dependent on the concentration of cyanide present. At cyanide concentrations greater than 1 ppm, a titrimetric procedure is used, while samples containing less than 1 ppm are analyzed by a colorimetric method.

NOTE: The methods described here are suitable for use only in the laboratory. Several other methods are available, some of which may be used in the field. However, the results obtained must be carefully interpreted, subject to the limitations of the particular test selected.

Precision and Accuracy

Method	Range of Application	Sensitivity	Accuracy	Precision
Titrimetric	>1 ppm	0.1 ppm	5%	± 2%
Colorimetric	0.01 - 1.0 ppm	0.01 ppm	10%	± 10%

NOTE: The figures given for accuracy and precision are average values. Deviations from these values are to be expected for very high or very low concentrations.

The species measured by the tests is the cyanide ion, CN^-, but the results are expressed as HCN. Only those forms of cyanide which are broken down by the particular distillation procedure used are included in the result reported.

Time of Analysis

A single analysis for free cyanide requires 90 minutes. However, sixteen analyses per day can be completed when the samples are tested in batches.

The determination of total cyanide must be done on an individual sample basis. The procedure is lengthy, requiring about one-half day per sample.

ANIONIC DETERGENTS
(as Alkyl Benzene Sulphonate (A.B.S.)

The presence of detergents in natural waters usually indicates contamination by domestic wastes. While A.B.S. is not toxic to most biota at low levels, it can be objectionable because of the foaming it may cause.

Sampling

Conventional sampling equipment is satisfactory, although care must be exerted to avoid contamination from any detergent used in cleaning this equipment.

Method

Methylene blue, which reacts with both A.B.S. and L.A.S. as well as a number of other organic compounds to produce a blue-coloured salt, is added to the sample. The blue salt is extracted with chloroform (it is more soluble in chloroform than in water) and the intensity of the blue colour, which is proportional to the concentration, is determined by a spectrophotometer. The test reacts equally to A.B.S. and L.A.S., and both are detected by this method together in an aggregate total, expressed in terms of an equivalent concentration of A.B.S. alone.

Precision - ± 10%

Accuracy

The test is subject to interference by a number of different compounds but the great majority of these cause a positive effect. Therefore, the reported value often represents a maximum possible concentration.

Interpretation

Samples which do not produce any foam when shaken vigorously contain less than 0.5 mgms per 1. This is the objective for natural waters, and it is not necessary to request A.B.S. analysis on samples if shaking does not induce a perceptible foam.

The results include both A.B.S. and the recently introduced "linear" forms L.A.S., although pure A.B.S. is used to calibrate the test and the results are expressed in these terms.

Cost

A single routine determination costs about three dollars.

ETHER EXTRACTABLES

Pollution by organic compounds is becoming more serious as the scale of heavy organic chemical industries, such as oil refining, meat packing, dairies, etc., increases. The oils, fats and greases in the waste discharges from these industries can greatly increase the oxygen depletion rate in the receiving waters, and if slicks are formed, they hinder oxygen uptake from the atmosphere. The ether extractable test is designed to give a measure of the amount of fats, oils and greases in water.

Sampling - A 40-ounce sample is required for this test alone and duplicate samples must be collected if other tests are required. A glass bottle with a foil-lined cap should be used, as any rubber or plastic caps, etc., may release extraneous organic compounds and often make further identification of pollutants impossible. The sample must be clearly labelled "ETHER EXTRACTABLE ONLY".

Samples can be preserved by refrigeration or freezing but most chemical additives can cause changes in the composition of the organic material present. If samples consist of more than one liquid phase, then clear instructions must be given as to whether ether extractables are required on the aqueous layer, the total sample or the organic (oil) layer. Natural material, such as twigs, leaves, etc., are to be excluded as much as possible since organic materials can be extracted from these as well.

Method - An aliquot of the homogenized sample is acidified and extracted with a chloroform/ethyl ether mixture. The extract is evaporated until the residue comes to a constant weight upon any further drying. The weight of the residue is related to the original aliquot in order to obtain an ether extractable in ppm. Volatile compounds, such as solvents, are lost in this procedure. The concentration range can be varied by changing the aliquot size. Sensitivity is about 1 ppm, but accuracy and precision are very dependent on the sample type. The test is only meant to be a rough guide to the amount of oils, fats and greases present.

Interpretation - While the test is intended to measure oils, fats and greases, there are many other organic compounds, such as resin acids, waxes, phenols, that dissolve in the solvent and thus contribute to the final result. Basic compounds are not extracted from the acid solution and therefore are not included in the reported result. The test does not measure the total organic concentraiton, and if an identification is performed on the extracted material, it will not necessarily be an exact indication of what is present in the raw water. If anything other than a rough guide to the indicated organic pollutants is required, it should be explained on the sample request sheet and/or discussed with the analyst.

Time of Analysis - A single test requires about one full day, but 8 to 10 determinations can be performed in a batch.

FLUORIDE

Fluoride is beneficial in preventing dental cavities. The fluoride concentrations in domestic water supplies throughout Ontario are monitored to ensure that the OWRC objectives are met: 1 ± 0.2 mgms per L for artificially fluoridated water and less than 2.4 mgms per L for natural fluoride. The upper limit has been set because of potential tooth mottling above this level.

Sampling

Conventional sampling equipment is adequate. Fluoride concentrations are stable with time, and special precautions are seldom required.

Method

The Alizarin Colorimetric Standard Method[1] previously used is now being replaced by the fluoride ion electrode method. This electrode produces a voltage potential relative to a reference electrode which is related to the fluoride concentration via a calibration curve. The principle of operation is analogous to the potentiometric measurement of pH.

Numerous studies[2] have shown that, with care, the electrode test is fully equal to the colorimetric methods and distillation of the sample to eliminate interferences is reported to be unnecessary.

Precision and Accuracy

Precision and accuracy are expected to be at least equal to the ± 0.1 ppm achieved previously. High concentrations of alumimum cause interference and the pH must be near neutrality. Compensations can be made in either case, but it is helpful to laboratory staff if warning of extreme pH or high aluminum concentrations is given. Warning should also be supplied if the fluoride content is likely to be high (above 1.5 ppm), since dilution procedures are required in this case.

Interpretation

Colorimetric kits employed in water works laboratories can give slightly biased results. The degree of color development obtained at the plant may not be the same as that originally used to calibrate the standards supplied with the kit. These results may therefore consistently yield somewhat lower values (occasionally higher) than is actually present. Monitoring the actual dosage added in pounds per hundred thousand Imperial gallons is the most reliable data in this case. By allowing for the original raw water fluoride content, etc., this method may be used to establish a ratio between readings obtained by the kit and actual fluoride levels (i.e., a reading of 0.8 may actually mean 1.0 is present).

Cost

A single measurement will likely cost less than one dollar, a substantial improvement over the previous costs, including distillation, which ranged up to five dollars per test.

References:

(1) Standard Methods for the Examination of Water and Wastewater, 12th Edition, American Public Health Association Inc. New York (1967).

(2) An Evaluation of Some Methods for the Determination of Fluoride in Potable Waters and Other Aqueous Solutions. W.T. Crosby, A.L. Dennis and J.G. Stevens. Analyst 93 643 (1968).

HARDNESS - CALCIUM AND MAGNESIUM

The total hardness or "soap-consuming power" of a water is mainly imparted by the presence of calcium and magnesium, and to a lesser, usually insignificant, degree by other metal ions. These minerals react with soap to form insoluble "curds" (as in bath water) and materially reduce the efficiency of washing procedures even when detergents are used. Hardness is usually reported in terms of an equivalent concentration of calcium carbonate alone.

Sampling - Conventional sampling equipment is adequate. Sample bottles must be filled to the top and tightly sealed to prevent loss of carbon dioxide. Calcium carbonate and other salts may precipitate if the carbon dioxide is lost and they are difficult to redissolve without adding acid which would invalidate other required analyses. Refrigeration is not necessary and the samples must not be frozen

Method - The sum of the calcium and magnesium concentrations is measured by titration at pH 10, using E.D.T.A. (ethylenediaminetetraacetic acid) and Eriochrome Black T indicator. The method is described in detail in Standard Methods (1) Calcium carbonate is used to standardize the hardness titration procedure, so the results are reported as mgms of calcium carbonate per liter, even though they include any magnesium present in the sample.

Calcium is determined on a second aliquot of the sample by titration with E.D.T.A. at a higher pH, using a different indicator (Murexide (1)) which is sensitive only to calcium. The result is reported as mgms per liter as calcium.

The magnesium concentration, reported as mgms per liter of magnesium, is determined by calculation from the difference between the total hardness and the calcium concentrations.

Precision and Accuracy - Total hardness can be measured from 10 mgms per liter as $CaCO_3$ and up with a precision of ± 5% and an accuracy of ± 5% or ± 5 mgms per liter, whichever is greater.

Calcium and magnesium concentrations above 2 mgms per liter can be measured with a precision of ± 5% and an accuracy of ± 5% or ± 2 mgms per liter, whichever is greater.

Interpretation - Hardness has often been measured as a matter of historical record and as a general indication of the mineral content of a given water supply. Calcium and magnesium are not harmful to humans and are important in water supplies primarily because they interfere with efficient laundering and cause "lime" buildup in heating systems and other related problems.

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Cost - A single hardness or calcium determination costs about one dollar.

Reference: (1) Standard Methods for the Examination of Water and Wastewater - 12th edition, American Public Health Association, Inc. 1967.

CHLOROPHENOXY ACETIC ACID-TYPE HERBICIDES

This class of compounds, commonly used as herbicides, are active as defoliants for broadleaf plants. The main problem posed by these compounds is that of the tastes and odours they can impart to water supplies at levels in the fractions of a part- per-million. They also decompose to chlorophenols, which are also often present as impurities from their manufacture. These compounds (chlorophenols) have taste thresholds of 1 - 2 ppb. This class of compounds includes: 2.4-D, 2,4,5,-T, silvex and 2,4-DB. They are often applied as derivatives (esters, amines, salts) of the free acid. It is preferable to know the particular derivative used before an analysis is started.

Sampling - Only water samples are normally accepted for these analyses. Samples should be at least 40 oz, taken in a clean solvent-rinsed bottle with a Teflon-lined cap, labelled "Herbicides Only - Freeze". These compounds are broken down very rapidly to chlorophenols. Thus, unless very high concentrations (10 ppm) are suspected, analysis must be performed within one day of suspected contamination. Cooling can delay breakdown. Sediments can adsorb this type of herbicide. Samples should, therefore, be as clear as possible. NO PLASTIC CONTAINERS.

Method - Current methods for the determination of 2,4-D type herbicides involve methylation, prior to cleanup by column chromatography, then determination of the methyl esters by gas-liquid chromatography.

Interpretation - Evaluation of the significance of results must be carried out individually, in the light of the previous history of the sample.

Range - Extends up to 0.50 ppm by dilution. Further extended by taking smaller sample aliquots.

Sensitivity - 0.3 - 1.0 ppb, dependent on individual acid concerned.

Precision - ± 6%

Accuracy - Recovery studies give an average of 92% recovery.

Expenses - A single test requires at least 12 man-hours over a period of three days.

TOTAL IRON

Because of the instability of the various forms of iron present in natural waters, the only reliable test for iron at the laboratory is total iron as Fe. This analysis includes an acid-digestion step of sufficient severity to detect all forms of iron whether inorganic or organic, soluble or insoluble, ferric or ferrous, including iron present in silt.

Tests at the laboratory which attempt to differentiate the various forms of iron will give data which can be completely irrelevant to field conditions. Ferrous and ferric iron are inter-convertible, depending on dissolved oxygen content of the water. Slight changes in pH, such as occur during shipment and storage, can cause precipitation of iron. The tendency of iron to form relatively stable colloidal suspensions can lead to misinterpretation of dissolved iron results. In short, the forms of iron present in the sample on delivery are not likely to be similar to those present when the sample was collected.

Sampling - The sampler should be certain that the sample submitted for analysis will reflect the conditions he wishes to examine. For example, if the iron content of silt or other particulate matter is not to be included in the analysis, the sample should be settled or filtered and a portion of the supernatant or filterate submitted for analysis. Do not request tests such as ferrous iron or dissolved iron to be performed at the lab, since data obtained would be completely irrelevant to field conditions.

Method - A suitable aliquot of the sample is digested by heating in the presence of hydrochloric acid to dissolve all iron present. Hydroxylamine added to the digest converts the iron to the ferrous state which reacts at pH4 with o-phenanthroline to form a coloured complex. The intensity of colour is measured by means of a photometer and translated, through calibration charts, to total iron as Fe.

Precision and Accuracy - Techniques are being developed to permit detection of total iron at or below 0.01 ppm. Accuracy is dependent to a high degree on individual sample history. Precision of analysis at levels greater than 1.0 ppm is estimated as ± 5%. At present, precision at levels less than 1.0 ppm is estimated as ± 0.05 ppm.

Interpretation of Results - In certain cases, total iron results can be misleading. Iron precipitated onto the surface of the sample bottle during shipment, or iron present in heavily silted samples, may affect the results obtained. It should be noted that other methods exist that purport to determine "total iron" which do not include severe acid-digestion. The results obtained from these methods would be better described as total dissolved iron, or ferric + ferrous iron, or other such terms.

Cost - A single routine determination on a water sample will cost approximately two dollars.

KETONES

Ketonic materials are in wide use throughout the chemical industry in paints, paint thinners, solvents, adhesives, etc. Since all the lower members are soluble in water, spills can lead to fairly high pollution levels. These materials are quite toxic and can cause taste problems in water supplies.

Sampling

The ketones which are used in the above contexts are all quite volatile, and losses may easily occur. Sampling procedures must take this fact into account. Samples should be taken in a clean 40-ounce glass bottle, with a foil or Teflon-lined cap. The bottle should be well sealed, and cooled to prevent loss of volatile ketones. This will also prevent any bacteriological breakdown of the ketones.

Method

The ketones are separated and identified by gas liquid chromatography. The sample is injected directly into the chromatograph and checked against calibrated standards. Confirmatory wet chemical tests are available for certain ketones, together with spectroscopic determination if the ketone can be isolated.

Sensitivity

$<$1 ppm.

Accuracy and Precision

Dependent on sample type, interferences, etc.

Interpretation

Toxicity and taste thresholds for ketonic solvents are widely documented. Since treatment and recovery techniques for ketonic wastes are developed and in general use, high results indicate accidental spill or negligence.

Expenses

The time required to complete such a test depends on the complexity of the sample. To separate the ketones from a complex matrix might require several days.

LEAD

Lead enters surface and domestic waters in the effluents of various industrial and mining operations, or as a result of corrosion of lead pipes. Since lead is a serious cumulative poison which tends to be deposited in the bones, the acceptable limiting concentration of lead in drinking water is 0.05 ppm.

Special Sampling Recommendations - The most reliable analytical result is obtained if the sample is collected in a plastic bottle and acidified with nitric acid. A separate sample, exclusively for lead analysis, should be submitted when very low concentrations must be determined exactly.

Method - In order to obtain the lead in a form suitable for analysis, the sample is first digested with a nitric-hydrochloric acid mixture. The lead concentration is then determined by atomic absorption spectrophotometry, polarography, or colorimetry.

Precision and Accuracy

Method	Range of Application	Sensitivity	Accuracy	Precision
Atomic Absorption	0.18 - 20 ppm	0.18 ppm	1.26%	± 1.24%
Polarographic	0.1 - 20 ppm	0.1 ppm	5%	± 5%
Colorimetric	0.04 - 5 ppm	0.034 ppm	2%	± 4%

NOTES:

1. The AAS method is preferred because of its speed and reliability. There are very few interferences with this technique, while the other two methods are subject to many interferences.

2. If very low concentrations of lead must be determined exactly, please inform the laboratory and the sample will receive different treatment. For such analyses, separate samples must be submitted for Pb.

3. The species determined is lead ion, which is reported as ppm lead.

Time of Analysis - A single analysis for lead by the preferred atomic absorption method requires about three hours. However, 20 analyses per day can be completed when the samples are tested in batches. The polarographic and colorimetric methods require much more time for completion, and are used mainly for standardizations and control purposes.

Manganese Test

Since manganese is found only in low concentrations in natural waters, any unusually large amounts in water will generally be the result of pollution from industries such as iron, steel, paint, and glass-manufacturing. Manganese is not toxic, but even very low concentrations cause unpleasant tastes, staining of laundry and plumbing fixtures, and encourage the growth of some micro-organisms in treatment plants. Hence the acceptable maximum concentration of 0.05 ppm in drinking water has been based on esthetic considerations.

Sampling

The sample should preferably be collected in a plastic bottle and acidified with nitric acid. However, no acid should be added if both dissolved and suspended forms are to be determined.

Method

In order to obtain the manganese in a form suitable for analysis, the sample is first digested with a nitric-sulphuric acid mixture. The manganese is then determined by atomic absorption spectrophotometry (AAS) or colorimetry.

Precision and Accuracy

Method	Range of Application	Sensitivity	Accuracy	Precision
Atomic Absorption	0.04 - 5 ppm	0.04 ppm	0.2%	± 0.41%
Colorimetric	0.01 - 1 ppm	0.02 ppm	0.5%	± 5 %

The AAS method is useful in the majority of analyses, where extremely low sensitivity is not required. If sensitivity is crucial, the formaldoxime colorimetric method is used. However, it is subject to interferences by iron and possible other common water pollutants. For concentrations above 1 ppm, a direct oxidation to permanganate can be used. The range of application can be extended by dilution or concentration of the sample.

Time of Analysis

A single analysis for manganese by the atomic absorption method requires about three hours. However, twenty analyses per day can be completed when the samples are tested in batches. The colorimetric method requires more time for completion.

Nickel

The concentrations of nickel salts found in natural waters are very low. Therefore, if nickel is found in water, it is likely to be the result of an industrial discharge, with the most likely source being an electroplating shop. The toxicity to man is believed to be very low, and, to the present time, no maximum acceptable concentration in domestic water supplies has been specified.

Sampling

The sample should be collected in a plastic bottle and acidified with nitric acid. However, samples in glass containers are accepted.

Method

In order to obtain the nickel in a form suitable for analysis, the sample is first digested with a nitric-sulphuric acid mixture. Then the nickel is determined by atomic absorption spectrophotometry, polarography, colorimetry or gravimetry.

Precision and Accuracy

Method	Range of Application	Sensitivity	Accuracy	Precision
Atomic Absorption	0.10 - 15 ppm	0.10 ppm	1.2%	± 1.4%
Polarographic	0.5 - 50 ppm	0.10 ppm	5 %	± 5 %
Colorimetric	0.1 - 10 ppm	0.08 ppm	5 %	±10 %
Gravimetric	1.0 - 50 ppm	1 ppm	1 %	± 1 %

NOTE: 1) The atomic absorption method is recommended over both polarographic and colorimetric analyses, since it is apparently interference-free, accurate, precise and sufficiently sensitive.

2) The ranges of application can be extended by dilution or concentration of the sample.

Time of Analysis

A single analysis for nickel by the preferred atomic absorption method requires about three hours. However, twenty analyses per day can be completed when the samples are tested in batches. The polarographic and colorimetric methods require more time for completion.

NITRATES AND NITRITES

Nitrates (NO_3) and nitrites (NO_2) may serve directly or indirectly as nitrogen sources for plants and algae. Consequently, their concentration in surface waters is of importance because an overabundance of plants and algae interferes with most water uses and costly remedial measures may be required. There is also a danger of high nitrate concentrations causing illness in babies, and a drinking water objective has been set at 10 mgms per liter as nitrogen (or 45 ppm nitrate as NO_3). Nitrate and nitrite determinations are thus relevant tests, not only on effluents, but on surface waters and domestic supplies as well.

Sampling - Conventional sampling equipment is satisfactory; however, both compounds are perishable, so samples should be refrigerated or frozen when collected, and delivered to the laboratory as promptly as possible.

Method - The raw samples are filtered through glass fiber filters, and analyses are carried out with no further treatment. Nitrite concentrations are measured by the colorimetric diazotization procedure recommended in Standard Methods*. The nitrite reacts with sulphanilic acid and 1-napthylamine to produce an intense red color. The procedure has been automated by the Technicon AutoAnalyzer system. A portion of the sample is passed through a column of finely divided cadmium metal which reduces the nitrate to nitrite, and the nitrite test is repeated, thus measuring nitrite and nitrate together. The nitrate concentration is then calculated by subtraction. Results for both compounds are reported in mgms per liter (ppm) as nitrogen.

Precision and Accuracy - Nitrite concentrations can be measured in the range 0.002 to 0.030 mgm per liter, with a precision and accuracy of ± 0.003 mgms per liter. Nitrate concentrations can be measured in the range of 0.05 to 0.40 mgms per liter, with a precision of ± 0.04 mgms per liter and an accuracy of ± 0.05 mgms per liter. Concentrations above these limits are measured by diluting the sample with distilled water before analysis.

Interpretation - Nitrate is present in natural waters as a result of direct waste discharges and as the end product of oxidation of organic nitrogen by bacteria. It can be utilized by aquatic plants, and the concentrations in surface waters are highly variable due to the combination of natural processes which produce and consume it.

Nitrite is usually present in natural water as an intermediary in the bacterial oxidation of ammonia or reduction of nitrate under aerobic and anaerobic conditions respectively. Under either conditions, there are further conversions to nitrate or ammonia by bacteria, and, consequently, the significance of a given nitrite

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concentration can often only be established by relating it to measurements of both of these other forms. It is seldom found at concentrations above 0.03 mgms per liter.

Cost - A single measurement of either nitrate or nitrite costs about one dollar.

Reference: *Standard Methods for the Examination of Water and Wastewater - 12th edition, American Public Health Association, New York. 1967.

FREE AMMONIA AND TOTAL KJELDAHL NITROGEN

Free ammonia is undesirable in surface water because it is toxic to fish; exerts a high oxygen demand when converted to nitrite and nitrate by bacteria; interferes with chlorination procedures at water treatment plants and is a source of nitrogen for plants which can help promote excessive growth. It is rarely found in concentrations high enough to be harmful to humans.

The total Kjeldahl nitrogen measures the sum of the free ammonia and the "organic nitrogen" (amines, proteins, etc.). "Organic nitrogen" can thus be obtained as the difference between the free ammonia and the total Kjeldahl nitrogen results. The total Kjeldahl nitrogen value does not include nitrite or nitrate which may be present in the sample.

Sampling - Conventional sampling equipment is satisfactory. Ammonia is very unstable and is rapidly converted to other nitrogen compounds by bacteria, which obviously also changes the concentration of at least one other nitrogen form. Refrigeration is helpful but freezing is the preferred methcd of preservation.

Although the total Kjeldahl nitrogen concentration includes free ammonia, it is not as perishable because bacterial action will convert at least part of the ammonia to organic forms which will still be measured by the test. The proportions of free ammonia and organic nitrogen may change quickly but the sum of the two is not so variable.

Method - Free ammonia concentrations are determined colorimetrically by an automated procedure using the Technicon AutoAnalyzer. The color is produced by the products of the reaction between ammonia and alkaline phenol hypochlorite. Acetone is used as a catalyst. The method is as sensitive and precise as that recommended in Standard Methods (1) using Nessler reagent.

For the total Kjeldahl nitrogen test, an aliquot of the raw sample is digested with sulfuric acid and potassium persulfate which converts the organic nitrogen to ammonia. This digestion method is fully equal to the standard Kjeldahl digestion described in Standard Methods (1). The resulting ammonia concentration in the digest is then measured using a modification of the free ammonia test. Results for both compounds are reported in mgms per liter (ppm) as nitrogen.

Precision and Accuracy - Ammonia concentrations in the range 0.05 to 0.30 mgms per liter can be measured with a precision of ± 0.03 mgms per liter and an accuracy of ± 0.05 mgms per liter.

Total Kjeldahl nitrogen concentrations in the range of 0.1 to 0.9 mgms per liter can be measured with a precision of ± 0.1 mgms

... over

per liter and an accuracy of ± 0.2 mgms per liter.

Samples with concentrations of either parameter above the given maximum are diluted with distilled water until they fall within these ranges.

Interpretation - Ammonia is often an indication of contamination by raw or partly treated sewage; however, because of its rather short life in surface waters it may not reveal completely the extent of the pollution. Results must be interpreted with full allowance for the perishability of this form of nitrogen, both in situ and in the sample following collection.

Ammonia is often converted to organic forms by bacteria, particularly if there is a good supply of organic carbon, so the total Kjeldahl nitrogen value can be a better indicator of the effects of an ammonia input than the ammonia concentration alone.

There may be oxidation of ammonia to nitrite and nitrate, so that measurement of these two compounds, in addition to the total Kjeldahl nitrogen, may be required to trace the effect of a waste input.

Cost - A single ammonia determination costs about one dollar, and a total Kjeldahl nitrogen measurement costs about three dollars.

Reference: Standard Methods for the Examination of Water and Wastewater - 12th edition, American Public Health Association Inc., New York. 1967.

CHLORINATED HYDROCARBON PESTICIDES

The laboratory is equipped to analyze for a considerable range of chlorinated hydrocarbon pesticides. The following compounds can be handled routinely: Lindane, BHC, Heptachlor, Aldrin, Heptachlore Epoxide, Dieldrin, Endrin, DDT, DDD, and DDE.

Any water sample submitted for analysis for chlorinated pesticides will be analyzed for the above materials. Any other compound of this type suspected should be named specifically. The analytical procedure is quite lengthy, and it is a great help to the analyst if only the compounds suspected are requested for analysis. These pesticides have been widely used in agriculture and pest control and are now common environmental contaminants. Although they have a relatively low acute toxicity, they are cumulative in human, animal and other biological systems and long-term effects are not yet fully understood. These compounds often cause a slightly musty odour in water.

Sampling - Water samples should be taken in a solvent-rinsed clean glass bottle (40 oz) with a Teflon-lined cap. Any type of plastic container is not acceptable, as plastics will adsorb this type of pesticide very rapidly. A full 40-oz sample is required for this test. Since these compounds are readily absorbed onto clay particles, it is preferable to obtain as clean a sample as possible. It should be stated whether analysis is required on the raw sample or a filtered sample. Other types of biological sample can be accepted (fish, sediments, etc.), but prior discussion with the analyst is required for this type of sample. Please label samples "Pesticides Only - Freeze". Biological samples such as fish, etc., should be quick-frozen to prevent bacteriological degradation.

Method - Chlorinated hydrocarbon pesticides are routinely analyzed by GLC. Confirmation for reasonably high levels (0.1 ppm) of pesticides may be obtained using thin-layer chromatography. Interferences are removed in this case by preliminary liquid/liquid extraction and, if necessary, cleanup with column chromatography.

Interpretation - Must be made in the context of the individual sample.

Range - Upper limits completely variable by dilutions.

Sensitivity - 0.01 to 0.1 ppb, depending on which compound is analyzed for. This sensitivity requires a relatively clean water sample. As the degree of contamination rises, sensitivity drops off sharply.

Precision - ± 5% (average figure, many compounds are better than this)

Accuracy - ± 5% - ± 10%, variable for different compounds.

NOTE - Any analysis in this class should be discussed with the Branch before any sampling is undertaken.

Expenses - One analysis requires 25 - 30 man-hours spread over several days or even weeks, depending on the method selected and on the material to be analyzed. Confirmation tests are usually required, which is an additional one day's work for one technician.

pH

pH is a measure of the hydrogen ion concentration in water. Specifically, it is the negative logarithm of the free hydrogen ion concentration expressed in moles per liter. Thus, each change of one unit in pH corresponds to a 10-fold hydrogen ion concentration change. Neutral solutions have a hydrogen ion concentration of 10^{-7} moles per liter; therefore, the pH is 7.

pH does not measure the total amount of acidity (or alkalinity) in the water, since some may be in a combined form and therefore will not be included in the pH measurement of free hydrogen ions. The combined forms can still be released to react with bases. The commonest example in water is the bicarbonate ion, which can react with acids to form carbonic acid, or with bases to form carbonates and water.

Sampling - pH is very dependent on temperature, dissolved gas concentrations, chemical reactions, etc., and is one of the more perishable parameters routinely measured. All measurements should be made in the field if possible. Laboratory determinations are reported as "pH at the lab" and must not be regarded as necessarily being the pH at the time of sample collection.

Method - The most reliable method is the use of commercial pH meters, operated according to the instructions supplied with the instrument. Many dyes change color at specific pH values and can be used as "pH indicators" within restricted ranges. These dyes are appropriate for indicating a reproducible pH value during a titration but are not reliable for the exact determination of an unknown pH. pH papers, impregnated with these dyes are even less reliable and should not be used for dilute solutions, i.e., nearly all water samples.

Precision and Accuracy - The precision and accuracy of pH meters depends on the quality (and cost) of the instrument. The meters in common use are precise and accurate to within ± 0.1 pH units. This can be increased to ± 0.01 with a good meter if great care is used.

pH indicators are only reliable to within about ± 1 pH units, and papers may be inaccurate by an even greater amount.

Cost - Measurements can be made in the laboratory for a very low cost, less than one dollar. Equipment for field use costs several hundred dollars initially, but is inexpensive to operate.

PHENOLS

Phenols are compounds having one or more hydroxy groups attached directly to an aromatic ring. This class contains countless compounds, ranging from simple phenol or carbolic acid to complex polyphenols, such as tannins and lignins. In water pollution control, the term phenols is applied only to the simpler phenols, which can be steam distilled. However, since in the methods used phenol itself is used as a standard, it should be realized that all routine phenol results are in terms of a phenol equivalent and must be regarded as the lowest value for phenolic content.

Phenolic compounds are often responsible for taste and odour problems in water, at levels as low as 1 - 2 ppb. Chlorophenols are particularly bad in this respect and are quite toxic to fish. These materials are easily formed during chlorination processes and therefore close control is often necessary.

Sampling

Phenols samples should be taken in clean 40-oz bottles, with foil-lined caps. Samples on which a wide range of other tests are required should be taken in duplicate, one being labelled "Phenols Only". Phenols are not very stable to oxidation or bacterial attack, especially in low concentrations. Phenols analyses should therefore be carried out as quickly as possible after sampling. Otherwise, samples should be preserved, as in Standard Methods, with copper sulphate and phosphoric acid. Refrigeration is also desirable. High concentrations of phenols (>100 ppm) will act as disinfectants and thus are relatively stable towards bacteria.

Methods

Phenols are routinely analyzed by three methods, one volumetric (iodometric) and two colorimetric methods. The scope of these methods is described below. Other techniques available for special cases are: gravimetry, gas chromatography, IR and UV spectorphotometry.

Method	Range of Application	Sensitivity	Precision	Accuracy
Iodometric Titration	Above 100 ppm	1 ppm	± 2%	(Depends (
Gibbs	0-120 ppb*	2 ppb	± 10%	(on type (of
4 Amino-Antipyrene	0-150 ppb*	5 ppb	± 5%	(phenols (present

*The range may be extended by dilutions.

In all methods used, reducing and oxidizing agents and a series of other organics will interfere, producing high or low results. For suspected interferences, one or more of the following procedures may be employed: chemical screening, extraction, or steam distillation. Results are reported indicating the method used and any preliminary procedures used.

Interpretation

Due to the different chemical reactions used for various tests, values obtained for a particular sample may differ from test to test.

The iodometric method is based on the bromination of the ortho and para positions (relative to the phenolic hydroxy group) on the aromatic ring. It is obvious that if either or both positions are already occupied, less or no bromination can occur. For more complex molecules, a given bromine value may actually represent a phenolic content several times that calculated. Any other compounds reacting with bromine (i.e., unsaturated compounds, aromatic amines, reducing agents) would produce the opposite effect, giving a calculated phenol value considerably higher than the actual amount present.

The 4-amino-antipyrene method, presently accepted as the standard method, and the Gibbs test, are both based on the coupling of a phenolic compound with a potential chromophore in the para position. Neither reaction will occur if this para position is occupied, unless the substituent is sufficiently labile to permit removal under the reaction conditions. Examples of this type of substituent are chlorine and carboxyl. Due to differing compositions of phenols, the final colour produced will vary. Many other non-phenolics with similar coupling ability will also produce coloured compounds. Examples are aromatic amines and some fatty acids.

These condensation reactions are influenced by several parameters such as pH, temperature, solvent systems, reducing and oxidizing agents. Interferences may be positive or negative and may affect the colour, varying from orange to deep blue. Since phenolic compounds are usually present as mixtures, all kinds of colours can be developed. Meaningful results will, therefore, require considerable knowledge of the composition of such mixtures.

Although distillation, extraction and chemical screening eliminate most of the interferences (non-volatile compounds, aromatic amines, water soluble reducing and oxidizing agents), some compounds (e.g., fatty acids) will follow the same route as the phenols. Also, the differences due to the varieties of phenols cannot be eliminated by screening. These differences affect the various methods differently; thus, results obtained by different methods for different phenolic compounds and expressed as carbolic acid could be quite far apart.

Comparisons of phenolic concentrations in samples taken at the same source are, however, possible, although the results do not necessarily represent the absolute quantity of phenolic compounds present.

Note:

The identification of individual phenols is a complicated procedure. Identification of phenols and chlorophenols on thin-layer chromatography is possible, using known standard compounds and various selective colour reagents. The position of certain peaks on a spectrophotometric curve and their shifts with varying conditions may also be used to characterize various phenols. Gas chromatographic separation and identification is also possible, but this is a long and expensive procedure. Requests for identification of phenolic compounds should, therefore, be limited to the minimum necessary.

Expenses

Nearly 50 direct determinations can be done per day by one technician using the Gibbs method, but this is reduced to about 30 if distillation is required, and to 8 - 10 for complete screening. The 4-AAP test requires more technician time but extends over a shorter time interval. Separation and identification of specific phenols is very time consuming and may require several days.

SOLUBLE PHOSPHORUS

The soluble phosphorus content of a sample is that fraction which will pass through a filter and will react chemically with the reagents used to determine the concentration of orthophosphate yielding a positive test response.

It is generally accepted that some organic and even particulate forms can react similarly to orthophosphate and, for this reason, the results are often referred to as "soluble reactive phosphorus", which removes the implication that the test measures only orthophosphate.

Sampling

Conventional sampling equipment is adequate. There is evidence that this parameter is very perishable; therefore, the samples should be refrigerated or frozen immediately after collection. A sample of 250 mls is sufficient for both soluble and total phosphorus tests.

Method

The sample is filtered through a glass fiber filter which has a pore diameter of 2 - 4 microns. The molybdenum blue orthophosphate analysis is applied directly to the filtrate. The method has been adapted for use on the Technicon AutoAnalyzer. Results are now reported in milligrams of phosphorus per liter. Before April 1, 1969, the results had been expressed in ppm of phosphorus as PO_4.

Precision

± 0.003 milligrams per liter or ± 10% of the reported value, whichever is greater.

Accuracy

Within the laboratory, the accuracy and precision are generally the same, but the effects of perishability and the difference of opinion regarding what is actually detected by the test make it impossible to give any estimates of over-all accuracy.

Interpretation

The meaning of this parameter has been left in some doubt by a number of researchers (Rigler and Fitzgerald). They have shown that:

a) particulate matter which can pass through pore sizes of 0 22 microns can alter the result. (This laboratory has been unable to confirm this finding for Great Lakes samples);

b) the soluble phosphorus concentration can change rapidly with time after collection, unless adequately preserved.

Anyone making conclusions based on soluble phosphorus results should be acquainted with the various interpretations made of such results.

Cost

When performed routinely by automated methods, the cost is nominal. Since the entire group of nutrient tests are performed simultaneously, an individual test cost is not calculable.

References

Rigler, F.H. The Phosphorus Fractions and the Turnover Time of Inorganic Phosphorus in Different Types of Lakes. Limnol and Oceanogr 9 511 (1964).

Fitzgerald, G.P. and S.L. Faust. Effect of Water-Sample Preservation Methods on the Release of Phosphorus from Algae. Limnol and Oceanogr 12 332 (1967).

TOTAL PHOSPHORUS

Phosphorus is an essential plant nutrient and is believed to play an important role in the deterioration of the quality of natural waterways by promoting an overabundance of plants. It occurs in natural and waste waters in several different chemical combinations, such as orthophosphate (PO_4), organic phosphates and polyphosphates. Since most or all of these forms can eventually be used by plants and animals, determination of the total phosphorus concentration is more relevant than measurement of individual phosphorus compounds.

Sampling

Conventional sampling equipment is adequate, and since the total quantity of phosphorus is measured, the test is usually not affected by perishability of individual compounds. Refrigeration and freezing are accepted methods of preservation. Since extremely low concentrations of phosphorus are significant, sampling containers must be of the utmost cleanliness to prevent any residual detergent from contaminating the samples.

Method

All forms of phosphorus in the sample are converted to orthophosphate by digestion with sulphuric acid and potassium persulphate. Very few if any phosphorus compounds are resistant to this treatment.

The digested sample is then analyzed for orthophosphate using the phosphomolybdate colorimetric method which has been adapted for use on the Technicon AutoAnalyzer.

The results have been reported as mgms of PO_4 (phosphate) per liter prior to April 1, 1969. From April 1, 1969 on, the results will be reported in milligrams of P (phosphorus) per liter (parts per million P). The conversion factor is $PO_4 \times 0.326 = P$.

Range

The minimum detectable concentration is 0.002 ppm. Samples with high concentrations are diluted until they fall within the range of the instrument which has an upper limit of 0.20 ppm.

Precision - ± 0.003 milligrams per liter or ± 10% of the reported value, whichever is greater.

Accuracy - usually equal to the precision; however, this test is known to be adversely affected by some interferences and in these cases the accuracy may decrease to ± 0.030 milligrams per liter. High concentrations of iron (greater than 1 ppm) may precipitate iron-phosphorus complexes, rendering it difficult to obtain a representative aliquot from the sample bottle and to obtain reproducible results.

Cost

When performed routinely by automated methods, the cost is nominal. Since the entire group of nutrient tests are performed simultaneously, an individual test cost is not calculable.

Silica

Silica and silicon are very abundant in nature. Together, they are present in sand and a variety of minerals and rocks. In water, silica is found in both soluble and colloidal forms, but in relatively small amounts because of its very low solubility. Effluents from some industries, notably glassmaking, will add to the level of silica in receiving waters. Only at very high concentrations does silica constitute a problem in drinking water, but lower concentrations may cause problems in thermo-electric plants, forming scale in boilers and on turbine blades.

Sampling

The sample should preferably be collected in a plastic bottle.

Method

If only the soluble or "molybdate-reactive" silica concentration is required on a clean sample, then the colorimetric method is used without prior treatment. When "total silica" is required, a bicarbonate digestion precedes the colorimetric test, or the gravimetric method is used after dehydration of the sample. Suspended materials and solid samples might require alkaline fusion prior to determination.

Precision and Accuracy

Method	Range of Application	Sensitivity	Accuracy	Precision
Colorimetric	0.02 - 1.0 ppm	0.02 ppm	± 10%	± 10%
Gravimetric	>20 ppm	0.2 ppm (mg/kg)	± 10%	± 10%

NOTE: The figures given for accuracy and precision are average values. Deviations from these values are to be expected for very high or very low concentrations of silica.

Sulphides, other reducing agents and a number of metal ions interfere in the colorimetric test.

The results are reported as silica (SiO_2).

Time of Analysis

Method	Time for One Test	Tests Per Day	
Colorimetric	20 min.	40 - 50	(not including the preliminary sample preparation work)
Gravimetric	1½ days	~ 6	

SODIUM AND POTASSIUM

Sodium and potassium are both very common in nature and occur in natural waters over a wide concentration range. Sodium is used extensively in industry, and large quantities of sodium chloride are applied to roads for ice control. Consequently, sodium can be found in high concentrations in industrial effluents and in road drainage in winter, as well as in sewage. Sodium is often the major cation component in brackish or saline well waters.

Patients on salt-free diets are advised to avoid consumption of water containing more than 50 mgms of sodium per liter. Waters softened by the ion-exchange process employed in domestic water softeners characteristically contain sodium in excess of this amount.

Potassium is normally present at much lower concentrations than sodium and, in general, seems to pose no danger to water users.

Sampling - Conventional sampling equipment is adequate. Both sodium and potassium concentrations are stable with time, except for alkaline samples which attack glass containers, releasing both sodium and potassium ions. Pyrex glass is more resistant than soft glass, but plastic bottles offer the best protection against contamination of alkaline samples

Method - Sodium and potassium concentrations are measured simultaneously on a flame photometer A specific volume of sample is vaporized in a flame, causing incandescence, and the intensity of a characteristic light emission line for both elements is measured The instrument has been calibrated to read directly in mgms per liter.

Precision and Accuracy - Sodium and potassium concentrations in the range of 0 to 25 mgms per liter can be measured with a precision and accuracy of ± 0.5 mgms per liter. Samples with concentrations above this range are diluted with distilled water.

Cost - Measurement of both the sodium and potassium concentration costs about one dollar per sample.

SOLIDS

Measurement of total, suspended and dissolved solids concentrations are traditional tests. An estimate of the organic fraction of the solids and of the organic content of sediments is obtained by heating the samples to 600°C in a furnace to burn off the combustible matter.

The suspended solids concentration relates to turbidity, and the dissolved solids concentration affects the specific conductivity, although there are no common factors for converting one to the other in all cases. A numerical relationship can often be obtained for a given area or type of water. Ontario rivers, free of industrial wastes, have a dissolved solids concentration of 0.65 ± 0.10 times the specific conductivity. The dissolved solids by weight concentration test has been largely superseded by the more accurate conductivity measurement.

Method

Total solids concentrations are determined by weighing the residue from a specific volume of the sample dried at 103 to 105°C. Dissolved solids are measured in the same way, except that the sample is filtered before withdrawing the aliquot.

The suspended solids concentration is measured either as the difference between the total and the dissolved solids or by filtering an aliquot and weighing the material collected. The latter method is used for low concentrations.

The results are reported in mgms of solids per liter of sample.

The loss on ignition results are reported in mgms of solids per liter of sample released by combustion at 600°C. The loss is due to oxidation of carbon and hydrogen, escape of water of hydration and loss of any other materials which are volatile below 600°C. Thus, the loss on ignition values represents the highest possible organic content. The actual organic content is lower than this by the amount of water, etc., released. In the case of clean waters, the loss on ignition is due almost entirely to loss of material other than carbonaceous.

Accuracy and Precision

Accuracy and precision are limited by the error in weighing the residue which is normally ± 1 mg. This gives a ± 100% error at the 1 mgm/l concentration. While this decreases with increasing concentration, random errors limit the accuracy of the test to no better than ± 5% at higher values.

Suspended and total solids are seriously affected by errors in obtaining a representative aliquot from the sample. This is particularly difficult to do for samples containing more than 10% solids by weight or material which settles rapidly, and is impossible when samples contain large solid particles.

Cost - An individual measurement costs about one dollar. A complete solids analysis costs three to four dollars.

TANNINS AND LIGNINS

Tannins and lignins are components of plant material and are found in surface waters as a result of the natural degradation of these materials. There are large amounts of tannins and lignins in the wastes from pulp and paper and leather industries. These pollutants will cause colour and undesirable tastes even in low concentrations.

Sampling - A filled, tightly sealed glass bottle of sample is preferred.

Method - Tannins and lignins are determined by a direct colorimetric method on an aliquot of sample supernatant which has received no prior treatment. The colour is produced by the product of the reaction between the phenolic groups in these compounds and tungsten salts which are added in the laboratory (Tyrosine reagent).

Precision and Accuracy - The test detects concentrations in the range of 0.5 - 4.0 ppm, with a sensitivity of 0.5 ppm. The precision is ±10%, with an accuracy of ±20%. The range of application can be extended by dilution of the sample.

Interpretation - Simple tannins and lignins are members of a large group of hydroxylated aromatic compounds, all of which react with the Tyrosine reagent, and the result which is reported includes all of these compounds. However, tannic acid is used as the standard to which the results obtained can be correlated. At present, no separation and individual determination of tannins and lignins is done in this laboratory. To convert the result to lignin, the value obtained as tannic acid should be multiplied by 2.5, since about 2.5 parts of lignin produces the same colour intensity as one part of tannic acid. Reducing agents interfere with this test

Time of Analysis - A single analysis for tannins and lignins requires about one hour; however, when the samples are treated in batches, approximately forty analyses can be completed in one day.

TURBIDITY

Clarity is one of the main criteria which the public uses in judging water quality, either for drinking or for recreational use. This makes the measurement of turbidity a much more valuable gauge of water quality than the suspended solids test, which measures only the weight of particles present in suspension and has little direct bearing on the appearance of the water. For instance, the presence of a few grains of sand or other coarse sediment, which produces a substantial suspended solids value, has little or no effect on the turbidity. It is recommended that field staff should make greater use of turbidity measurements in place of suspended solids tests.

Sampling

Conventional sampling equipment is adequate. Most water samples are not particularly perishable. Samples containing heavy particles with a tendency to settle immediately, or to coalesce, such as some river water and industrial effluents, may give unreliable results.

Method

An arbitrary scale is used to measure turbidity, defined as the depth to which a cloudy sample must be poured in a calibrated tube, to 'extinguish' the image of a standard candle light source, employing the Jackson Turbidimeter instrument. This defines the units for expression of results, 'Jackson Turbidity Units' (J.T.U.) or more simply 'Turbidity Units'. These are synonymous with the older terms 'Silica Scale Units', or ppm Silica, since these were also measured by reference to the Jackson Turbidimeter.

Other instruments may be calibrated by means of comparison with results obtained using the Jackson Turbidimeter. This laboratory is now employing Hach Model 2100 Turbidimeters in place of the Hellige instruments previously used. The Hach model measures turbidity through the amount of light scattered at right angles by the particles in the sample, as registered by a sensitive photomultiplier tube. Its major advantage over the Hellige instrument is an increased sensitivity of detection at low levels of turbidity.

Precision and Accuracy

Since readings cannot be obtained on the Jackson Turbidimeter below 25. J.T.U., there is no absolutely certain means of calibrating other instruments at these lower levels. Our tests to date indicate that Hellige readings are reliable down to 5 J.T.U., and Hach Model 2100 instrument results down to 2 J.T.U. Calibration at levels lower than this awaits the continent-wide adoption of an arbitrary standard material for the preparation of reliable low level reference samples of turbidity.

Thus, we have no means of calibrating our Hach instruments below 2 J.T.U., and if our readings conflict with those obtained by other laboratories, there is no way in which either laboratory will be able to validate its results. Other laboratory results will thus have to be accepted as equally valid in this range. Above this range, precision and accuracy are claimed to be ± 2.% by the manufacturer of the Hach instrument.

Interpretation

OWRC Drinking Water Objectives have recently been decreased from 5 J.T.U. to 1 J.T.U., in recognition of the increased efficiency of water treatment now possible. (Note the limits of precision above).

Turbidity in large volumes of water is noticeable at levels above 5 J.T.U., and many members of the public complain that the water is 'dirty' or 'cloudy' in such cases, particularly if they desire to swim or fish. Turbidity is certainly the main criterion which citizens employ in assessing the quality of water, and surveys of water quality should always include turbidity measurements.

Cost

Operating costs for the Hach Turbidimeter are expected to be less than one dollar per test.

Zinc Test

Zinc occurs abundantly in rocks and ores and is readily refined into the pure metal for use in electroplating, dye-manufacturing and other industries. Because zinc is beneficial to body growth and has no known adverse physiological effects, except at very high concentrations, the limiting factors which determine the acceptable maximum concentration in a water supply are taste and appearance. Concentrations of zinc in excess of 5 ppm may impart a bitter taste and a milky appearance to the water and may cause a greasy film when the water is boiled.

Sampling

The sample should preferably be collected in a plastic bottle and acidified with nitric acid. However, no acid should be added if both dissolved and suspended forms are to be determined.

Method

In order to obtain the zinc in a form suitable for analysis, the sample is first digested with a nitric-sulphuric acid mixture. The zinc is then determined by atomic absorption spectrophotometry, polarography, or colorimetry.

Precision and Accuracy

Method	Range of Application	Sensitivity	Accuracy	Precision
Atomic Absorption	0.013 - 1.5 ppm	0.015 ppm	0.4%	± 0.9%
Polarographic	0.2 - 10 ppm	0.2 ppm	5 %	± 5 %
Colorimetric	0.2 - 5 ppm	0.17 ug.	5 %	± 10 %

NOTE:
1. The ranges of application can be extended by dilution or concentration of the sample.
2. The atomic absorption method is preferred over the other two. It is simpler, more rapid, and very sensitive.
3. Few interferences with zinc analysis by atomic absorption are known. However, very high (0.5% or over) calcium, sodium, or potassium concentrations can interfere, and if such species are suspected, please inform the laboratory.

Time of Analysis

A single analysis for zinc by the preferred atomic absorption method requires about three hours. However, twenty analyses per day can be completed when the samples are tested in batches. The polarographic and colorimetric methods require more time for completion.

Date Due
